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Correlation effects and electronic structure of $\text{Gd}@C_{60}$

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Abstract

We have investigated the electronic structure of $\text{Gd}@C_{60}$ using *ab initio* calculations, photoemission and resonant photoemission (constant initial state spectroscopy). In comparing our calculations based on the local spin density approximation and the Hubbard model description with the observed photoemission spectra, we conclude that Gd 4f states exhibit enhanced correlation energies. These correlation energies have values larger than those normally observed in metallic gadolinium and gadolinium compounds. We attributed the enhanced correlation to the diminished screening of the encapsulated Gd. Both calculation and experiment confirm a strong hybridization between the valence states of Gd and the C 2p states of the fullerene cage.

Water-soluble Gd-based endohedral metallofullerenes ($\text{Gd}@C_{82}(\text{OH})_x$, $\text{Gd}@C_{60}(\text{OH})_x$, and $\text{Gd}@C_{60}[\text{C}(\text{COOH})_{10}]$) have been studied extensively as a result of their novel electronic and structural properties [1–3]. These Gd-based metallofullerenes are regarded as a possible new generation of magnetic resonance imaging (MRI) contrast agents not only because of their excellent proton relaxivities (which are greater than those of commercially available MRI contrast agents) but also because they may serve as a safer alternative. The toxic Gd ions are completely encaged inside the fullerenes and appear to be inhibited from dissociation and oxidation under physiological conditions, but the

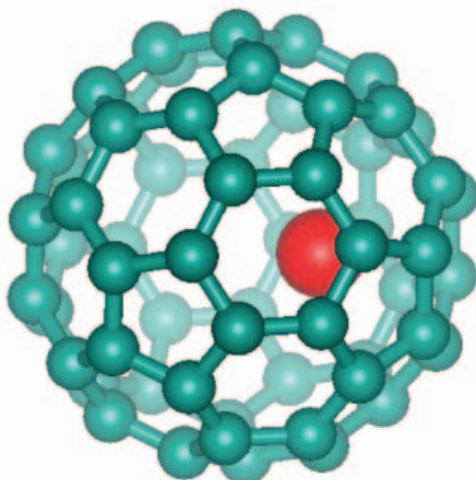


Figure 1. Optimized structure of Gd@C₆₀.

cytotoxicity of water-soluble fullerene species, particularly C₆₀, is a sensitive function of surface derivatization [4].

Recently, Lu *et al* performed an *ab initio* study of the structural and electronic properties of Gd@C₆₀ [5, 6]. They established that the Gd is located at an off-centre position within the cage, with a short side Gd–C bond length of 2.38–2.41 Å, similar to that predicted for Gd@C₈₂. At the same time Gd transfers most of the 5d and 6s electron weight to the fullerene cage molecular orbitals, resulting in a charge density shift towards the carbon cage. The bonding between Gd and C₆₀ may thus be considered predominantly ionic in nature. The Gd@C₆₀ in the ground state has a multiplicity of $M = 7$, from the half-filled Gd 4f shell, resulting in a large magnetic moment, whose coupling to the cage 2p will be discussed.

Here, we explore the electronic properties of Gd@C₆₀ through a comparison of theoretical modeling with photoemission spectroscopy and resonant photoemission (constant initial state spectroscopy). We demonstrate that the on-site repulsion for Gd 4f states is stronger than in the bulk Gd, while strong hybridization between Gd 5d and 6s states and the carbon molecular orbitals is observed.

We performed first-principle calculations based on the optimized structure of the endohedral gadofullerene (shown in figure 1). We used the projector augmented wave method with a general gradient approximation (the so-called PAW-PBE version [7, 8]) and applied corrections in the form of a Hubbard U (correlation energy) to the Gd 4f states [9]. Although the Gd 4f states are fairly well localized in the case of pure Gd and its compounds, nonetheless, on the theoretical side, it is generally understood that methods such as the local spin density approximation (LSDA) usually underestimate the on-site repulsion of the 4f states. LSDA-based calculations predict that the Gd 4f states have binding energies about 4 eV below the Fermi energy E_F for majority spin and 2 eV above E_F for minority spin, in the absence of a correlation energy correction.

We have varied the Hubbard on-site repulsion in the LSDA + U scheme, in this study, *i.e.* varied the value of U from 6 to 7.6 eV. For Gd@C₆₀, we found that a correlation energy of $U = 7.6$ eV, in the model calculations, provides the best agreement with experiment, in particular with the position of the photoemission features with strong Gd 4f weight.

The photoemission studies were performed using a hemispherical electron energy analyzer with combined resolution (with the monochromator) of 90–200 meV and an

angular acceptance of $\pm 1.5^\circ$, with the monochromatic light dispersed by a 3 m toroidal grating monochromator at the Center for Advanced Microstructures and Devices (CAMD) in Baton Rouge, Louisiana. Linearly polarized light-dependent photoemission was taken with light incidence angles of 45° and a 70° , while collecting the photoelectrons along the film normal (to preserve the highest point group symmetry). Polarized light-dependent photoemission was used to explore the possibility of preferential molecular orientation, by exploiting symmetry and selection rules.

To ensure sample purity, the Gd@C₆₀ was studied by photoemission by adsorbing multilayer thin films from sublimed powder on Au(111) substrates, cooled well below room temperature (to hinder desorption and decomposition under ultra-high vacuum conditions). The Gd@C₆₀ powder was obtained from TDA Research Corp., synthesized with greater than 90% purity using procedures described elsewhere [10].

In figure 2(b), we show the photoemission of a Gd@C₆₀ film, sufficiently thick for suppression of almost the entire signal from the Au(111) substrate. To establish which valence band features contain strong weight from the Gd 4f states, valence band photoemission spectra were completed at much higher photon energies (100–140 eV), to enhance the 4f photoemission cross section. We find that Gd 4f states reside at a -10 to -11 eV binding energy, indicated in higher-resolution photoemission spectra taken at 20 eV photon energy, shown in figure 2. These findings are consistent with earlier studies of Gd@C₈₂ [11–13] and represent much higher 4f binding energies than those observed for Gd metal (typically -8.6 eV). These results can be compared with theory (figure 2).

The energy diagram and broadened densities of states (DOS) are shown together with the photoemission spectrum in figure 2. Notice that we have a good match, starting from the singly occupied molecular orbital (SOMO) at the Fermi energy to all the shallow core states of Gd, *i.e.* 5s, 5p, and 5d, as well as for carbon. In addition, there is a shift of the energy scale between the calculated densities of states and photoemission data of about 1.3–1.6 eV. This shift is probably due to the underestimation of the band gap in our calculations, which is a well known problem of the LSDA method, and such shifts in energy are not unusual.

As just noted, when fitting the Gd 4f states, we had to adopt a correlation U to be 7.6 eV to obtain a reasonable match with the photoemission spectra. This value of $U = 7.6$ eV for Gd@C₆₀ is larger than the value 6.7 eV commonly used in the gadolinium compounds and certainly a somewhat larger value than is typical for Gd metal. A value of $U = 6.7$ eV is the value found to be most appropriate in the examples of the GdX (X = N, P, As, and Bi) compounds [14], but is not appropriate here. The larger U value of 7.6 eV for Gd@C₆₀ is expected because the encapsulated Gd atoms experience less screening than Gd atoms in bulk metal or even in rare earth pnictide or chalcogenide compounds. Also, charge transfer, from Gd to the cage, will shift the photoemission binding energies to larger values.

The HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) gap is 0.15 eV in the majority spin state and 0.35 eV in the minority spin state from the model PAW-PBE calculations. These values are larger in PAW-PBE than those in LSDA calculations [5, 6]. The seven Gd 4f electrons remain intact as core states, while the remaining three electrons (5d¹, and 6s²) strongly hybridize with carbon states. The highest occupied molecular orbital, with some 5d electron weight, is singly occupied at zero temperature. It is important to note that if the Gd atom is simply shifted off-centre towards any hexagon of the carbon cage, this state is found to be doubly degenerate. The competition between the structural distortion (the Gd placement off-centre) and electronic structure, however, causes a local Jahn–Teller distortion with symmetry C₁ that in turn lifts the degeneracy, and changes the Gd–C bond lengths slightly and lowers the energy of the system by less than 0.3 meV. This is in the limit of the accuracy of the calculations, which usually involve Gaussian broadening of the states. This broadening effectively mimics

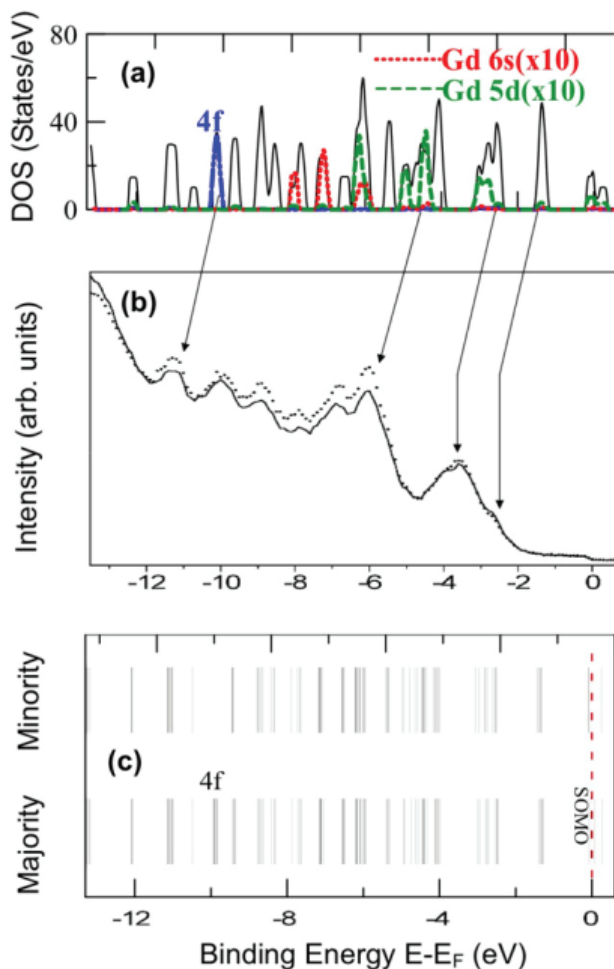


Figure 2. (a) Total density of states, with $U = 7.6$ eV, for the endohedral fullerene $\text{Gd}@C_{60}$. Notice that 4f states (blue curve) are located at -10 eV. The Gd 5d (dashed (green) curve) and 6s (dash-dotted (red) curve) states are mixed with the carbon states. (The magnitude of the Gd 5d and 6s states is multiplied by 10 to help the eye.) (b) Photoemission of the occupied molecular orbitals of $\text{Gd}@C_{60}$, following multilayer molecular adsorption on a gold substrate. The photoemission spectra were taken with a photon energy of 20 eV for a 45° light incidence angle (solid line) and a 70° light incidence angle (dashed line). (c) Energy diagram of the spin majority and minority states.

higher temperature effects. If Gaussian broadening of the states is used with σ larger than 0.05 the ground state is found to be doubly degenerate with two-fold symmetry. The Gd states are strongly hybridized with the MO of the carbon cage: in figure 2, we show that the Gd 5d partial DOS (dashed (green) curve) contribute significantly to states with energies between E_F and 8 eV below E_F , while the Gd 6s states (dashed-dotted (red) curve) are distributed from 5 to 10 eV below E_F . Based on the population analysis, we found that the charge transfer from the Gd ions to carbon molecular orbitals is significant (natural population analysis shows about $2.4e$), as previously discussed [6, 11, 12].

The placement of the gadolinium off-center in the C_{60} cage in our model calculations (figure 1) is supported by the photoemission results. We have observed that there is a light polarization dependence; namely the photoelectron intensity is more intense in the region of

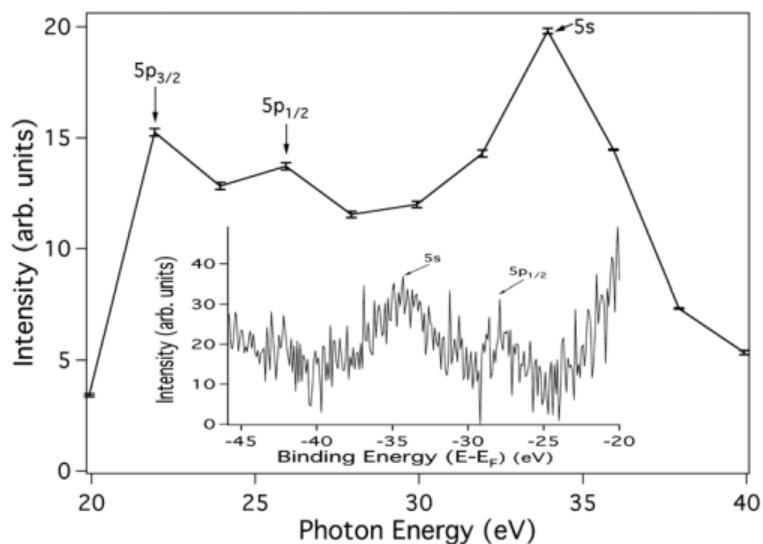


Figure 3. The photoemission intensities at 6 eV binding energy for $\text{Gd}@C_{60}$, as a function of photon energy. The photoemission intensities are seen to increase at photon energies that roughly correspond to the Gd 5s and 5p shallow core edges, indicating a resonant photoemission process that includes Gd. In the inset, a photoemission spectrum, taken at higher photon energy, 95 eV, indicates the binding energies of the Gd 5s and $5p_{1/2}$ cores in $\text{Gd}@C_{60}$.

6 eV binding energy, with the \mathbf{E} vector of the incident light placed more along the surface normal, i.e. a light incidence angle of 70° (solid curve, figure 2(b)), than for photoemission taken with the \mathbf{E} vector of the incident light placed more along the surface, i.e. a light incidence angle of 45° (dotted curve, figure 2(b)). This indicates that the $\text{Gd}@C_{60}$ molecular species was partly oriented on the gold substrate [15]. Since the C_{60} molecular high-symmetry states (hybridized with Gd as discussed below), with respect to the molecular axis through the Gd atomic displacement direction, are found at this binding energy, this photoemission result is consistent with the electric dipole moment, resulting from the Gd atom being “off-center” in the C_{60} cage, mostly lying along the surface normal.

To demonstrate that the valence band features contain more than the C_{60} molecular orbitals, that is to say that the molecular orbitals contain Gd weight as well as the C_{60} molecular orbitals, consistent with the calculations (figure 2(a)), resonant photoemission or constant initial state spectroscopy studies were undertaken. We measured the photoelectron intensity, at about 6 eV binding energy (from the Fermi level), for various photon energies (as shown in figure 3). The background contributions were taken out, so that a direct comparison could be made at each photon energy, following the flux normalization. It is clear that there are three resonant enhancements in the photoemission intensity, from this -6 eV binding energy initial state, occurring at photon energies corresponding to the binding energies of the Gd 5s (36 eV), Gd $5p_{1/2}$ (28 eV) and Gd $5p_{3/2}$ (21 eV) shallow cores. In the inset, we present a photoemission spectrum taken at higher photon energy (95 eV), illustrating the Gd 5s, Gd $5p_{1/2}$ shallow cores from $\text{Gd}@C_{60}$, providing a consistent picture of a resonant photoemission process of excitation from these shallow cores to a bound state, but with a final state identical to that resulting from direct photoemission from the molecular orbitals at -6 eV binding energy, leading to the resonant photoemission [16, 17]. These photoemission resonances at photon energies close to the Gd shallow core binding energies are indications that the features near -6 eV in the photoemission spectrum have strong Gd weight. Furthermore, the shift of Gd-weighted molecular orbitals towards -6 eV and -9 to -10 eV, in the photoemission, argues in favor of very strong hybridization of

Gd states with states of the C_{60} cage. This entire picture is consistent with the theoretical analysis, which indicates an overlap of the states of Gd and the carbon cage (see figure 2). The cage hybridization with Gd can also be inferred from the effective magnetic moment providing a moment of $6.0 \mu_B$ obtained in the present calculations, compared to crystalline or atomic Gd at $7.3 \mu_B$ and $8 \mu_B$ respectively. The antiferromagnetic exchange between the Gd and the cage diminishes the total moment by about $1.25 \mu_B$, due to the carbon cage.

In conclusion, we have studied theoretically and experimentally the electronic structure of $Gd@C_{60}$. From comparing the photoemission spectra with theoretical calculations, we found good agreement. We observed a strong correlation effect, which manifests itself in the shift of the Gd 4f state to higher binding energy, and correlation energy U of about 7.6 eV, which is larger than normally detected in gadolinium compounds. We attributed that to a lack of screening of the encapsulated Gd. In addition, we notice prominent resonant intensity features, due to the Gd 5s and 5p cores in the resonant photoemission spectra taken from 6 eV below the Fermi level, which indicate strong hybridization between the Gd valence states and the fullerene cage. All the above phenomena are explained using the LSDA + U calculation.

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